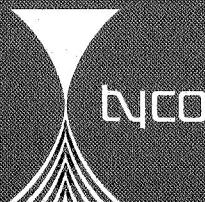Development of Cathodic Electro-
catalysts for Use in Low Temperature
H_2/O_2 Fuel Cells with an
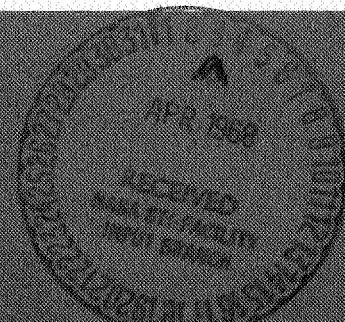Alkaline Electrolyte

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DEVELOPMENT OF CATHODIC ELECTROCATALYSTS FOR USE

IN LOW TEMPERATURE H_2/O_2 FUEL CELLS

WITH AN ALKALINE ELECTROLYTE

by
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J. Parry
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DEVELOPMENT OF CATHODIC ELECTROCATALYSTS FOR USE IN LOW TEMPERATURE H_2/O_2 FUEL CELLS WITH AN ALKALINE ELECTROLYTE

CONTRACT OBJECTIVES

The research under contract NASW-1233 is directed towards the development of an improved oxygen electrode for use in alkaline H_2/O_2 fuel cells. The work is being carried out for the National Aeronautics and Space Administration, with Mr. E. Cohn as technical monitor. Principal investigators are Dr. J. Giner and Dr. J. Parry.

CONTENTS

ABSTRACT

The eight station test rig for studying the life of cathode catalysts is now operational. The preliminary tests carried out on two stations demonstrated that the moisture control system was effective. Only minor modifications (replacement of vent rate control valves) were necessary after the 150 hour tests. Three stations were then started on long-term tests. The catalysts tested are 60 Au/40 Pd, a Tyco platinum electrode, and an American Cyanamid AB-40. The latter electrode is intended to provide a standard for comparison of the cell behavior operating conditions and performance with the well established information on the commercial electrode. These cells have logged 200 hours without any difficulties. The performance levels that are being maintained for a cell voltage of 850 mv are Au/Pd = 5.6 amp, Tyco Pt black = 4.8 amp, and AB-40 = 4.5 amp.

The Bureau of Mines' catalysts tested were the alloys, carbides, and nitrocarbides of 3 Ni/Au, Ni/3 Au, 3 Ni/Pt, Ni/3 Pt, and 3 Ni/Ag; 3 Pd/Ag and Pd/Ag catalysts were also examined. The silver palladium alloys showed very high currents (> 300 ma/cm^2 at 750 mv $\underline{vs}$. RHE) but were much less active than Pd/Au or Pt catalysts at 950 mv $\underline{vs}$. RHE where the currents were ~ 5 ma/cm^2. The best activity from the Ni/Au catalysts was 32 ma/cm^2 at 750 mv, and 28 ma/cm^2 from the Ni/Pt. A Ni/Ag catalyst gave an activity of 70 ma/cm^2 at 750 mv $\underline{vs}$. RHE. This level of performance is disappointingly low, particularly for the Pt based catalysts. The order of activity was in all cases alloy > carbide > nitrocarbide. Both the Ni/Au and Ni/Pt alloys showed the apparently anomalous behavior of the nickel rich alloys being the more active.

Finely divided titanium nitride and titanium gold were prepared by an evaporation technique. Neither showed significant activity.

The preparation of Au/Pd catalysts and the fabrication of large electrodes for life testing was continued.

A mathematical approach to the operation of the PTFE bonded electrode is outlined in this report. The objective of the approach is to be able to predict the effect on electrode performance of readily measurable characteristics of the catalyst such as the exchange current, the surface area per unit volume, the microporosity, macroporosity, pore size distribution and agglomerate size, and the physical characteristics of the system (solubilities, diffusion coefficients, conductivity, etc.). The first calculations for O_2 reduction at a Pt electrode, assuming $10\,\mu$ dia. agglomerates, gave good agreement with experimental measurements but also indicated that the depth of penetration of the agglomerates was less than 1%.

I. CATALYST LIFE TESTING

The eight station test rig for studying the life of cathode catalysts for O_2 reduction is now operational. The catalysts are tested as PTFE bonded electrodes in a matrix electrolyte cell. The individual test station is conventional in design (see Figs. 1, 2, and 3), providing for the control and measurement of gas pressures and flow rates and for the collection and measurement of the water produced. Particular attention was paid to carrying out the tests under realistic conditions but under circumstances (not necessarily feasible in a practical cell) that avoid the more common failure modes of a H_2/O_2 cell. Decay in performance can then be directly attributed to the cathode catalyst.

An example of this approach is the means of maintaining the water balance, probably the most critical variable in the operation of a matrix cell. This is achieved by having a large reservoir of electrolyte immediately behind the anode (see Fig. 4). The reservoir defines the water vapor pressure in the anode gas space (i. e. no presaturation is necessary) and therefore controls the water content of the electrolyte trapped in the matrix. Since the reservoir electrolyte concentration cannot change very rapidly even with relatively high H_2 flow rates, the water vapor pressure can be regarded as constant for relatively long periods of time (say several hours). An effective water balance can then be maintained by comparing the total amount of water removed with that produced (calculated from the current time curve) and by making the necessary adjustments in the gas flow rates. A further refinement is the provision of porous nickel wicks from the electrolyte reservoir to the matrix. Then, in the event of loss of KOH from the matrix (e. g. lost as a result of gross deviations in the water balance which result in drowning), the KOH may be replaced by diffusion through the wicks.

The reservoir cell, therefore, simulates a free electrolyte system but without the associated interface problem, and has the advantage that it reduces the gas flow rate sensitivity of the water removal mechanism.
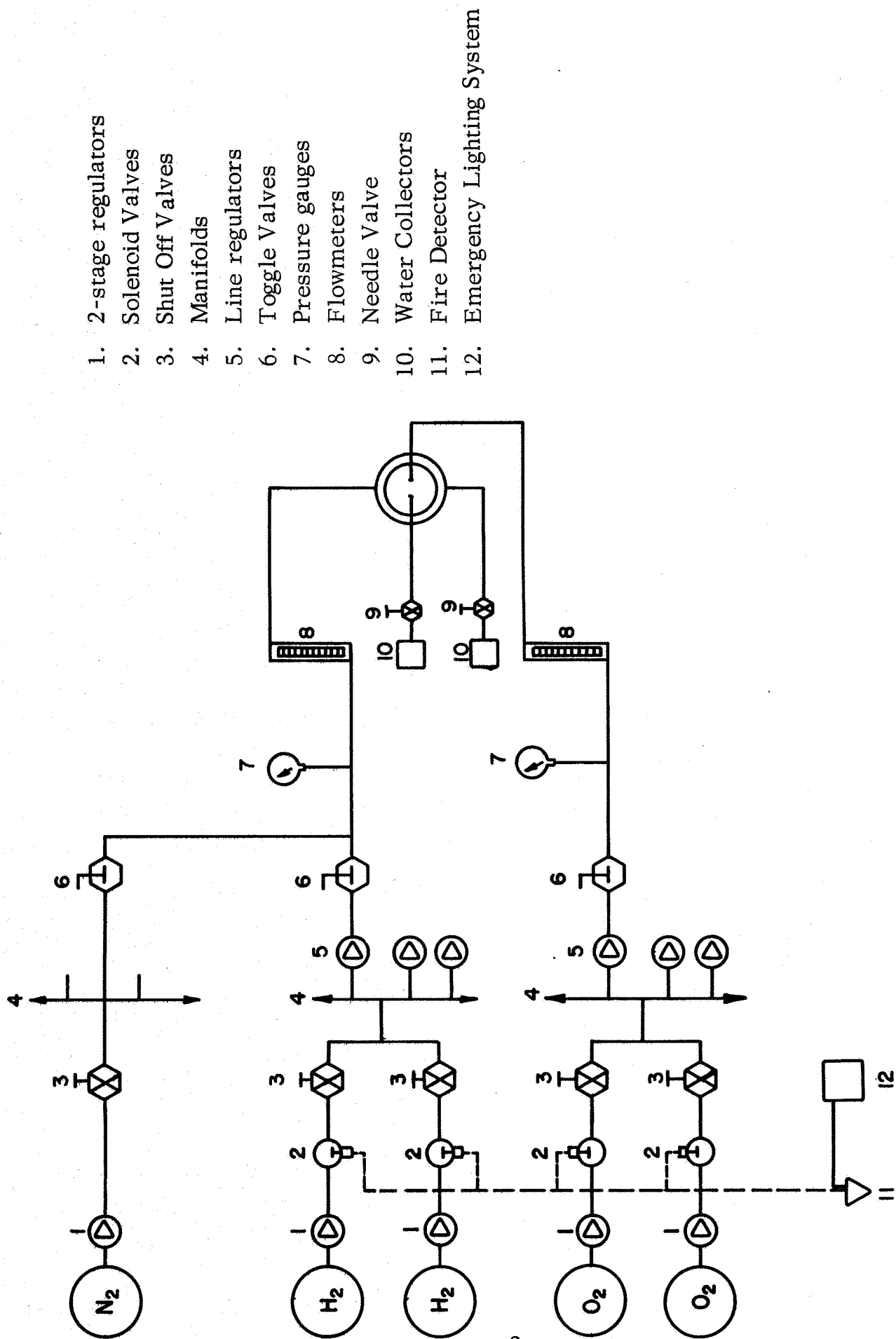
1. 2-stage regulators
2. Solenoid Valves
3. Shut Off Valves
4. Manifolds
5. Line regulators
6. Toggle Valves
7. Pressure gauges
8. Flowmeters
9. Needle Valve
10. Water Collectors
11. Fire Detector
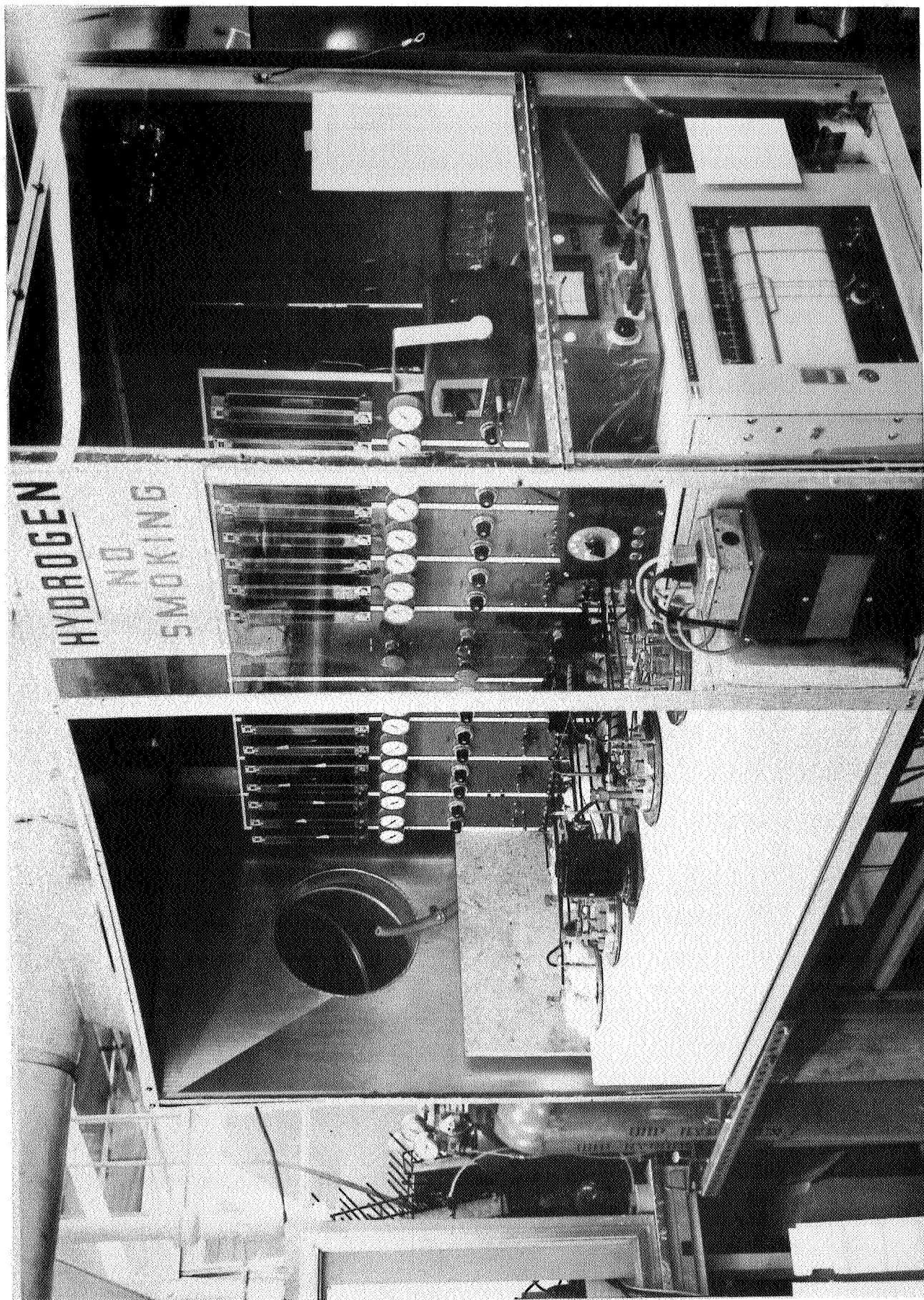12. Emergency Lighting System

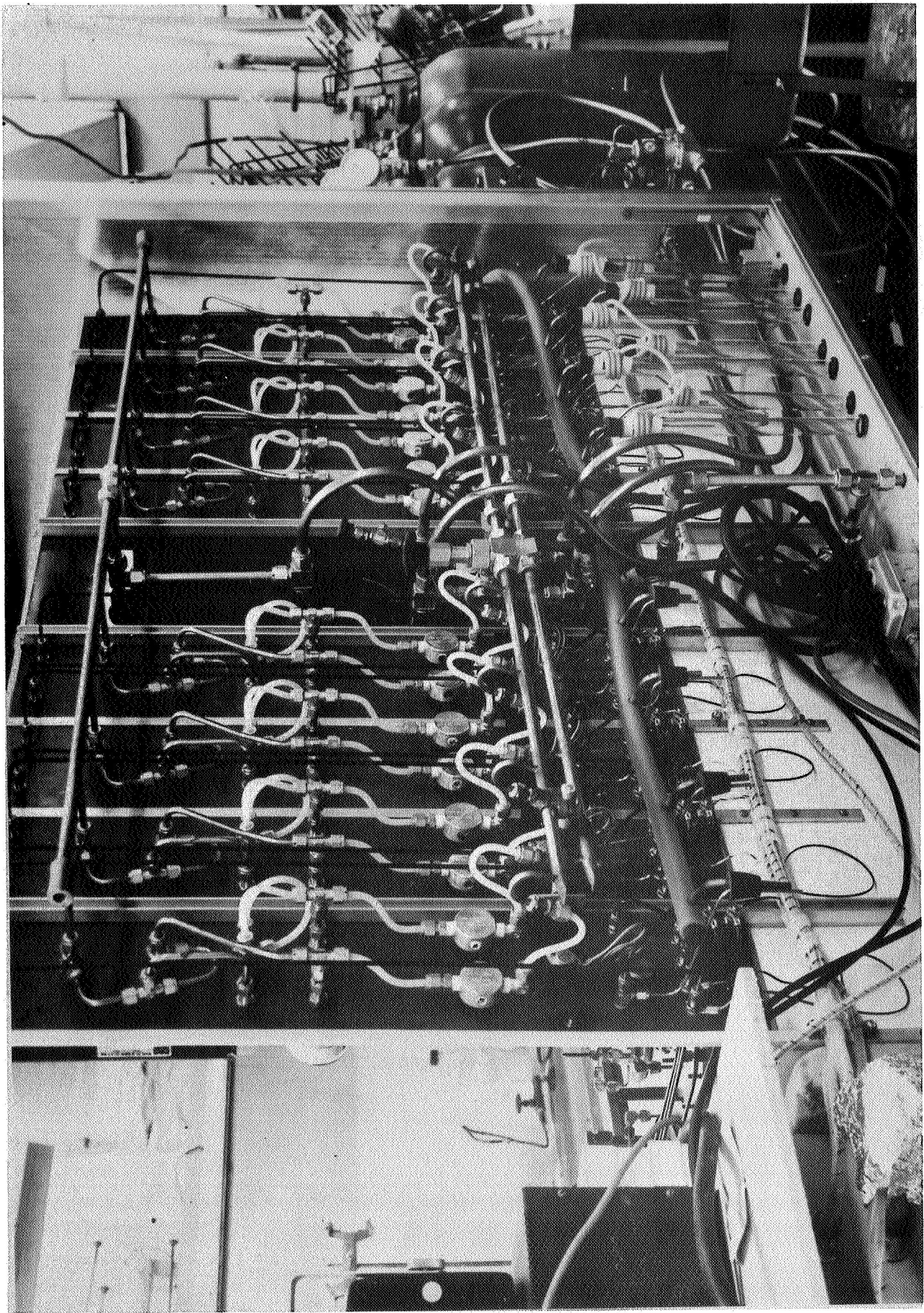Fig. 1 Flow diagram of test rig.

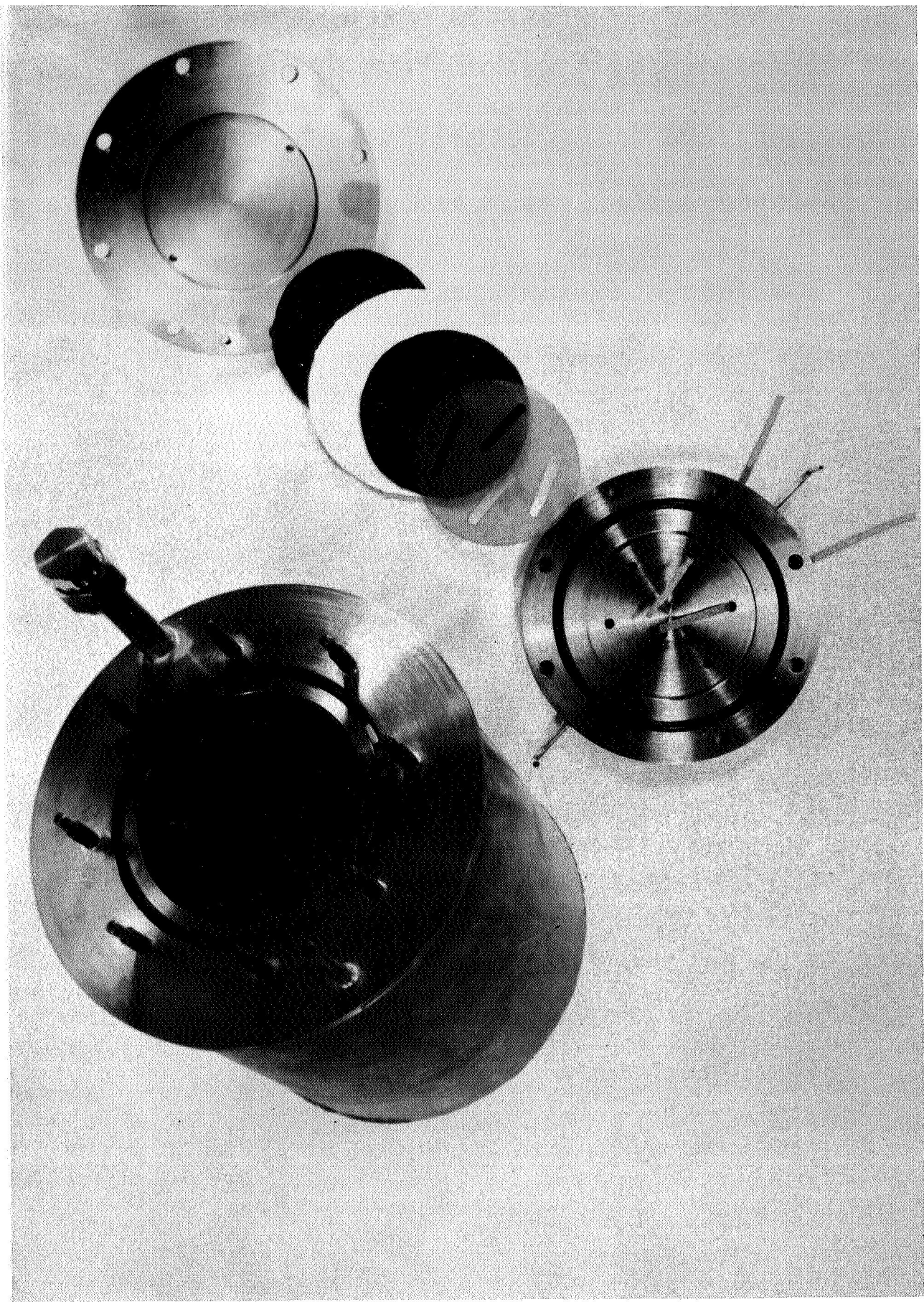- 2 -

Fig. 2 Test rig.

Fig. 3 Test rig – rear view

Fig. 4 Reservoir test cell - exploded view

The catalysts are being tested as PTFE bonded electrodes 3.14" dia. formed on gold plated expanded nickel screen. The electrolyte is 40% KOH and the cells are run at 80°C. In all cases the anode is a commercial platinum electrode (American Cyanamid AB-40). This electrode with a Pt loading of 40 mg/cm^2 on a gold plated nickel screen is specifically designed to give long life and reliability.

The catalysts to be tested include three palladium gold alloys (40%, 50%, and 70% Pd), three platinum osmium alloys (10%, 20%, and 30% Os), a high activity Pt black prepared at Tyco, titanium gold, and nickel-based catalysts (e.g. nickel carbide, nickel nitrocarbide, and nickel cobalt alloys).

The preliminary tests of the system and the commencement of extended tests are described below.

Preliminary System Tests. Two cells were set up initially, one with an American Cyanimid AB 4X cathode, the other with an electrode made at Tyco from a commercial platinum black (37 mg/cm^2). The anodes of both cells were American Cyanamid AB-40 electrodes.

Both cells were run with 40% KOH in the temperature range 77 to 79°C. The patterns of performance for both cells are shown in Figs. 5 and 6. The principal difference between the two life tests is that cell #2 failed three times during the course of the test, but was successfully restored to the original performance level by blowing out the cathode vent lines. This action removed large quantities of electrolyte (compared with the amount of water normally removed by the gas glow) and probably accounts for the difference between the theoretical and measured quantities of water shown in the plots in Figs. 5 and 6. The problem was considered to be due, in part, to the difficulty of controlling the low gas flow rates and the pressure differential across the cell with the needle valves originally fitted on the vent lines. These were replaced to alleviate this difficulty. It is also possible that the electrolyte accumulates in the cathode space because of some transport mechanism (e.g. electro-osmosis) that is a critical function of the structure and PTFE content of the electrode. This accumulation of electrolyte can
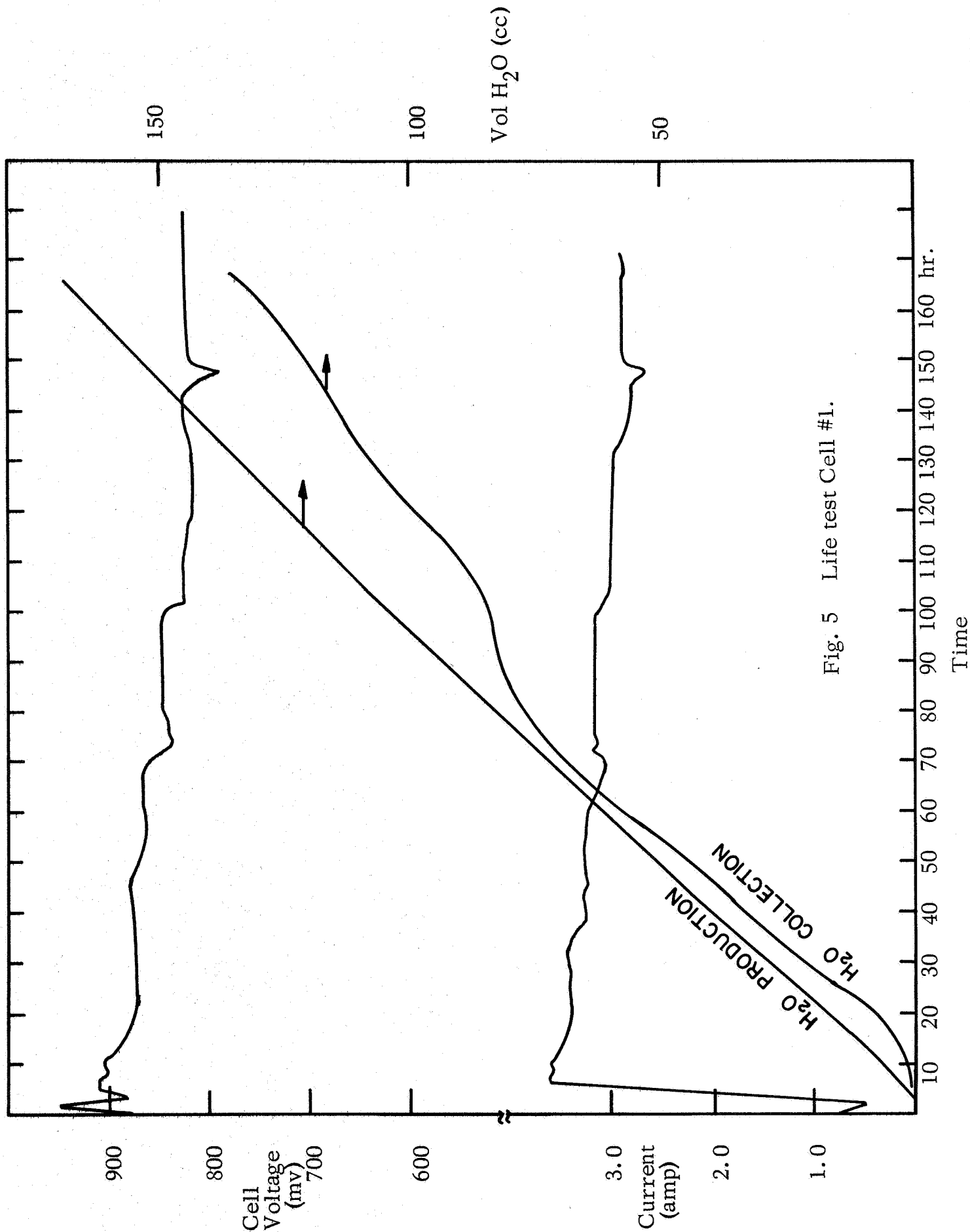
Fig. 5   Life test Cell #1.

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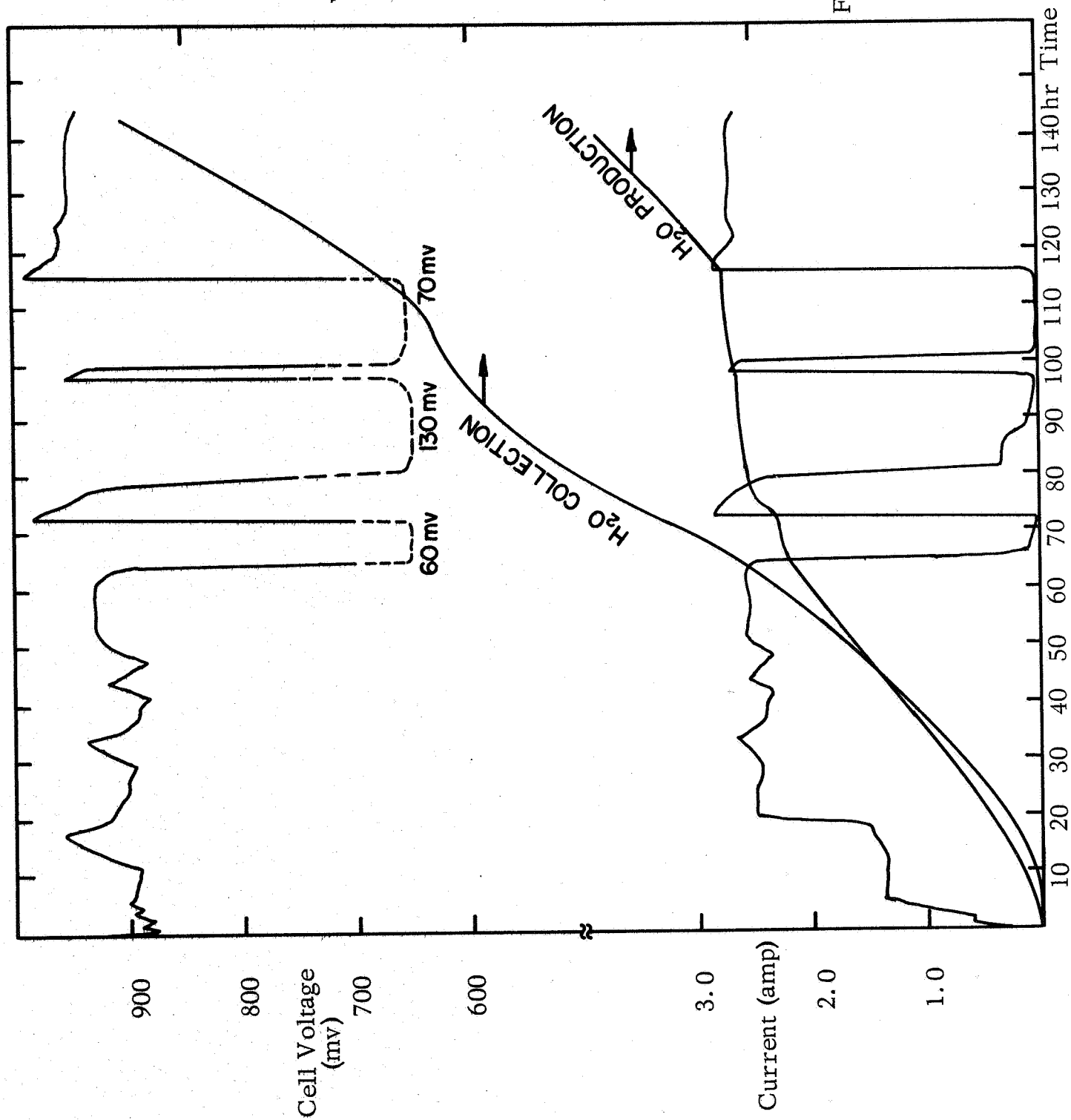
Fig. 6 Life Test Cell #2.

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usually be avoided by applying a pressure differential across the cell. This was difficult to control in the initial test because of the difficulties associated with the adjustment of the needle valves in the vent line.

Maximum current from the cells was < 3A until copper leads were used as the current carriers to the load device in place of the stainless steel tubing (the gas lines to the cell). To improve current collection at the cathode, the nickel screen current collectors and the cell back plate have now been gold plated. In order to make the modifications listed above, tests on cell #1 was terminated after 170 hours and #2 after 144 hours.

New tests were started with gold palladium and Tyco platinum electrodes and have logged 200 hours without any difficulties. The performance levels that are being maintained are Au/Pd 5.6 amp at 850 mv. Tyco Pt black 4.8 amp at 850 mv, and AB-40 4.5 amp at 850 mv. These tests will be reported in detail in a further report.

II. CATALYSTS PREPARED AT THE BUREAU OF MINES

The materials tested during this report period were the alloys, carbides and nitrocarbides of 3 Ni/Au, Ni/3 Au, 3 Ni/Pt, Ni/3 Pt, and 3 Ni/Ag; and the 3 Pd/Ag, and Pd/Ag alloys. The activation and details of the electrode preparation are listed in Table I. The silver palladium alloys 3 Pd/Ag and Ag/Pd showed very high currents ($> 300 \text{ ma/cm}^2$) at 750 mv vs. RHE but activity at 950 mv (of the order of 5 ma/cm^2) was lower than that observed with Pt or Au/Pd alloys. This is in accord with the results presented for solid electrodes of these alloys in the Fourth Quarterly Report of this contract. The 3 Ag/Pd alloys showed better, but still low, activity at 950 mv but the current at 750 mv was much reduced (190 ma/cm^2).

The Ni/Au alloys showed disappointing activity, with the Ni/3 Au alloys giving lower activity than the 3 Ni/Au alloys. This surprising result was reproduced in a re-examination at Tyco with electrodes of different PTFE content and in measurements made at the Bureau of Mines. The carbides and nitrocarbides of 3 Ni/Au were much less active than the parent alloy; the same compounds of Ni/3 Au were marginally more active (4 ma/cm^2 compared with 1 ma/cm^2 at 750 mv vs. RHE) than the alloy.

The Ni/Pt alloys showed a very much lower activity than might be expected for a Pt based catalyst. The series of materials showed the same pattern of activity, as has been described before, of alloy > carbide > nitrocarbide. As with the Ni/Au alloys the activity of the nickel rich alloy was greater than that of the Ni/3 Pt alloys. The 3 Ni/Ag catalysts were very similar in performance to the 3 Ni/Au catalysts.

TABLE I

BUREAU OF MINES CATALYSTS

| Electrode | | | | Activity[1] | | |
Catalyst	Induction	% PTFE	Loading mg/cm^2	ma/cm^2 at 950 mv	ma/cm^2 at 750 mv	ma/cm^2 at 600 mv
74 R (i) [2] 3 Ni/Au	No	30	44		32/32	55/54
74 R (ii) 3 Ni/Au	Yes	30	41		16/16	32/32
74 R (iii) 3 Ni/Au	No	30	48		20/25	38/40
74 R (iv) 3 Ni/Au	No	10	54		15/15	25/25
74 C (i) 3 Ni/Au C	No	30	38		14/13	24/25
74 C (ii) 3 Ni/Au C	Yes	30	41		17/19	32/35
54 NC (i) 3 Ni/Au NC	No	20	39		9/14	23/23
54 NC (ii) 3 Ni/Au NC	Yes	20	56		5/5	13/23
76 R (i) Ni/3 Au	No	10	90		1.0	1.0
76 R (ii) Ni/3 Au	Yes	10	90		1.0	1.0
76 C (i) Ni/3 Au C	No	10	94		1.0	1.0
76 C (ii) Ni/3 Au C	No	10	94		1.0	1.0
53 NC (i) Ni/3 Au NC	No	10	116		4/4	4/4
53 NC (ii) Ni/3 Au NC	Yes	10	111		1.0	1.0
79 R (i) Ag/3 Pd	No	10		5/5	375	(limiting current)
85 R (i) Ag/Pd	No	20	50	3.5/5	7300	(limiting current)
86 R (i) 3 Ag/Pd	No	20	48	9/18	205	(limiting current)

TABLE I (Cont'd.)

Electrode Catalyst	Induction	% PTFE	Loading mg/cm²	Activity[1] ma/cm² at 950 mv	ma/cm² at 750 mv	ma/cm² at 600 mv
80 R(i)[2]	3 Ni-1 Pt	No	30	41		25/30	55/58
80 R(ii)	3 Ni-1 Pt	Yes	30	45		28/32	53/54
80 C(i)	3 Ni-1 Pt C	No	30	47		16/18	36/40
80 C(ii)	3 Ni-1 Pt C	Yes	30	46		19/26	46/58
58 NC(i)	3 Ni-1 Pt NC	No	30	42		8/13	24/32
58 NC(ii)	3 Ni-1 Pt NC	Yes	30	62		8/8	18/19
82 R(i)	1 Ni-3 Pt	No	30	55		10/10	17/17
82 R(ii)	1 Ni-3 Pt	Yes	30	66		7/7	13/13
54 NC(iii)	3 Ni-1 Au NC	Yes	30	46		4/5.5	9/12
76 R(iii)	1 Ni-3 Au	Yes	30	34		2/2	3.5/3.5
76 C(iii)	1 Ni-3 Au C	Yes	30	39		2/2	3.5/3.5
53 NC(iii)	1 Ni-3 Au NC	Yes	30	39		1/1	2/2
79 R(iii)	1 Ag-3 Pd	Yes	30	57	3.5/5	275/307	
84 R (i)	3 Ni-Ag	No	20	28		28/29	51/51
84 C (i)	3 Ni-Ag C	No	20	40		10/9	22/20
61 NC (i)	3 Ni-Ag NC	No	20	53		Anodic	
84 R (ii)	3 Ni-Ag	Yes	20	30		70/75	137/140
84 C (ii)	3 Ni-Ag C	Yes	20	36		4/4	12/12
61 NC (ii)	3 Ni-Ag NC	Yes	20	46		Anodic	

(1) Activity expressed as current at decreasing potential
    Current at increasing potential

(2) Electrodes are numbered as follows: 80 R - Bureau of Mines' catalyst
    Identification No.

    (i) - Tyco Electrode Identification No.

III. CATALYSTS PREPARED AT TYCO

Four further preparations of Au/Pd 60/40 alloys were made and several electrodes tested in the continued approach to define the optimum preparative method for Au/Pd catalysts. Both these preparations were very similar to the previous best preparation which resulted in electrodes with an activity of 4.1 ma/mg at 950 mv. Neither of these preparations approached this activity. The principal difference between the two reactions described here is in the initial mixing of reagents. In preparation F8, a portion of the reactants was brought slowly to a pH of 8.5 in an attempt to induce nuclei formation prior to the growth stage in NaOH. This was omitted in preparations F9 and F10. There is a marked difference in activity of the catalysts (see Table II), indicating that these initial factors do influence activity.

The preparation HY-1 in which hydroxylamine was used as the reducing agent resulted in electrodes of quite good activity (4.5 ma/mg). Further preparations based on this method will be carried out.

Titanium nitride and titanium gold (Ti_3Au) were prepared as finely divided powders and tested as PTFE bonded electrodes. The preparation of the titanium nitride involved the evaporation of titanium metal in a N_2 atmosphere at 50 μ pressure. The titanium gold was evaporated from a wire into an inert atmosphere (Ar) at ~ 50 μ pressure. The titanium nitride was blue-grey in color; (stoichiometric TiN is a golden yellow). On electrochemical testing the electrode showed a small cathodic current and rapidly turned white. This was probably due to incomplete formation of TiN. Since the N_2 pressure during evaporation controls the condensation rate and therefore the particle size, it is unlikely that the stoichiometric form of TiN can be prepared in finely divided form using this method.

The evaporated Ti_3Au also showed low activity in both the tests carried out. The low activity could be due to separation of the components during the evaporation of the intermetallic compound. Titanium when oxidized could effectively isolate, in terms of conductive paths, the gold component of the catalyst so that even the expected activity of the gold was not observed.

<u>TABLE II</u>

TYCO CATALYSTS

Electrode	% PTFE	Loading mg/cm^2	Activity		ma/cm^2 at 600
			ma/cm^2 at 950 mv	ma/mg at 950 mv	
TiN (1) Evaporated Titanium Nitride	42	7.2			4.2/4.7 (1)
(11) Evaporated Titanium Nitride	52	7.7			3.3/3.5
Ti$_3$Au (1) Evaporated Titanium Gold	27	5.7			1.6/2.9
(11) Evaporated Titanium Gold	40	5.3			2/2
Pd/Au Evaporated 40/60 Pd/Au	27	44	40	0.9	
Pt (i) (2)	20	15.2	97	6.3	
Pt (ii) (2)	20	15.9	48	3.0	

(1)   Oxidized to white powder during test.

(2)   Small Pt electrodes cut from single large electrode.   (i) sintered in large furnace   (ii) sintered in regular furnace

Catalyst Preparation			Electrodes			Activity	
Initial Concentrations	Initial Volume	T°C	#	%PTFE*	Loading mg/cm²	ma/cm² at 950 mv	ma/mg at 950 mv
F-8 Pd-Au (40-60) Au - .05 M Pd - .033 M NaOH - 2.45 M HCOH - .56 M	1260	98	(i)	30(2)	23	5	.2
			(ii)	30(1)	42	5	.12
			(iii)	30(1)	45	60	1.33
F-9 Pd-Au (40-60) Au - .063 M Pd - .042 M NaOH - 2.4 M HCOH - .56 M	1000 ml	95	(i)	30(1)	41	90	2.2
			(ii)	20(1)	51	15	.3
			(iii)	15(1)	45	105	2.33
			(iv)	15(2)	58	66	1.14
			(v)	15(3)	44	78	1.8
			(vi)	20(1)	38	42	1.1
			(vii)	20(2)	34	36	1.1
			(viii)	20(3)	45	28	.6
			(ix)	25(1)	33	8	.24
			(x)	25(2)	32	12	.37
			(xi)	25(3)	35	13	.37
F-10 Au - .065 M Pd - 0.068 M NaOH - 5.4 M HCHO - 1.2 M	390	96	(i)	15	33	60	1.8
			(ii)	30	43	13	0.3
			(iii)	15	45	145	3.2
			(iv)	30	32	100	3.1
HY-1 Au - 0.1 M HONH$_2$.HCl - Sat.	125	20	(i)	20	22	100	4.5
			(ii)	20	23	56	2.4

(1) Sintered 250°C - 5 min   (2) Sintered 275°C - 5 min   (3) Sintered 300°C - 5 min

Table II (Cont'd.)

The two platinum catalysts (Pt (i) and Pt (ii) Table II, are samples of the same electrode preparation; (i) was sintered by our established method in the small sintering over, the other (ii), in the new oven designed to accommodate large electrodes. In the large oven the thermal mass has been kept to a minimum giving a warm-up time of 8 min to 275°C and cool-down time of 12 min. These times are greater than those of the small oven, but it is apparent from the results in Table II that in the case of Pt there is no detrimental effect. This was confirmed with the four large electrodes, also listed in Table III.

TABLE III

Performance of Large Electrodes

Electrode Catalyst[1]	Induction	% PTFE[2]	Loading mg/cm^2	Activity[1] ma/cm^2 at 950 mv	Activity[1] ma/mg at 950 mv
Pt-L(i) Engelhard Platinum	No	30	25	95	3.8
Pt-L(ii) Engelhard Platinum	No	30	21	116	5.5
Pt-L(iii) Engelhard Platinum	No	30	23	110	4.8
Pt-L(iiii) Engelhard Platinum	No	30	46	210	4.6

(1) All electrodes made on expanded nickel screen

(2) All electrodes sintered at 275°C for 15 minutes

IV. MATHEMATICAL STUDIES OF PTFE BONDED ELECTRODES

It is highly desirable to have a working model that allows one to predict the effect on electrode performance of readily measurable parameters and variables such as intrinsic activity of the electrocatalyst (i.e. exchange current, i_o), microporosity, macroporosity, surface area per unit volume, geometrical dimensions of the electrode, pore size, agglomerate size, gas solubility, diffusion coefficient, ionic conductivity, etc.

Attempts by several workers to solve this problem have contributed greatly to an understanding of the porous electrode, but their solutions are either based on unrealistic models or cannot be used as a predictive tool for experimental work.

In our model we assume an electrode with a double scale of porosities, i.e. with flooded catalyst agglomerates which contain channels (small pores) for ionic conductivity, and unflooded pores which serve for gas diffusion. One way of conveniently treating the problem without impairing its practical applicability is to assume that the flooded agglomerate is a porous cylinder of radius r_o and length h, in which catalyst particles and electrolyte are homogeneously dispersed in a microscopic scale. (Microporosity, θ, is defined as the volume of electrolyte per total volume of cylinder.) The porous cylinder is perpendicular to the external surface of the electrode. During operation, gas arrives at the cylinder in a direction perpendicular to its axis and diffuses to its center along the coordinate r with simultaneous bulk reaction on catalyst particles in the diffusion path. Ionic current is conducted in the direction x to the cylinder axis; electronic resistivity is assumed to be zero. The number of these cylinders per cm^2 of electrode (N) is related to a measurable macroscopic factor, which we will call macroporosity (β), by the expression $\beta = 1 - N \pi r_o^2$.

The local current density i (r, x), (current per unit of "real area") at a point (r, x) in the cylinder is assumed to be expressed by equation:

$$i = i_o \left[\frac{C\ (x, r)}{C_o}\ \exp\ \alpha\ z\ \eta\ (x)\ /\ \phi\ -\ \exp\ -\ (1\ -\ \alpha\ )\ z\ \eta\ (x)\ /\ \phi\ \right] \quad (1)$$

where

i_o = exchange current

α = transfer coefficient ($o < \alpha < 1$; usually $\alpha = 1 - \alpha \equiv \frac{1}{2}$)

z = stoichiometric number

T = absolute temperature

η = local overvoltage measured against a reversible reference electrode placed at point (r, x).

The main limitation introduced with this assumption is that the current is <u>directly</u> proportional to concentration. (In some cases the current could be proportional to some power of the concentration other than one.)

The diffusion of the gas in the cylinder (with a simultaneous bulk consumption given by $i\gamma/nF$, γ = surface to volume ratio) follows the 2nd Fick's law for cylindric diffusion:

$$\bar{D}\,\frac{\partial^2 C(x, r, t)}{\partial r^2} + \bar{D}\,\frac{1}{r}\,\frac{\partial C(x, r, t)}{\partial r} - \frac{i\gamma}{nF} = \frac{\partial C(x, r, t)}{\partial t} \quad (2)$$

($\bar{D}$ is the effective diffusion coefficient, which is affected by porosity and tortuosity).

At steady state:

$$\frac{\partial C(x, r, t)}{\partial t} = 0$$

and therefore:

$$\bar{D}\left\{\frac{\partial^2 C}{\partial r^2} + \frac{1}{r}\,\frac{\partial C}{\partial r}\right\} = \frac{i\gamma}{nF} = \frac{\gamma\, i_o}{nF}\left\{\frac{C(x, r)}{C_o}\,\exp\frac{\alpha z \eta(x)}{\phi} - \frac{(\alpha-1)z\eta(x)}{\phi}\right\}$$

$$(3)$$

Boundary conditions:

$$\frac{\partial C}{\partial r} = 0 \text{ at } r = 0, \quad C = C_o \text{ at } 4 = r_o$$

The solution of this equation for the r-variation of C is straightforward:

$$C = C_0 \exp - \frac{z \eta}{\phi} + \text{(the solution of the homogeneous equation}$$

$$\frac{\partial^2 C}{\partial r^2} + \frac{1}{r} \frac{\partial C}{\partial r} - \left[\frac{\gamma i_0}{n F \overline{D} C_0} \exp \frac{\alpha z \eta}{\phi} \right] C = 0 \left. \right) \quad (4)$$

The solution of the homogeneous equation can be expressed in terms of modified Bessel functions.

Since $\partial C / \partial r = 0$ $r = 0$, the solution for C is:

$$C = C_0 \exp - \frac{z \eta}{\phi} + k_1 I_0 \left(\left[\frac{\gamma i_0}{n F \overline{D} C_0} \exp \frac{\alpha z \eta}{\phi} \right]^{\frac{1}{2}} r \right), \quad (5)$$

where I_0 is standard notation for the modified Bessel function of zero order and k_1 is a constant.

k_1 is fixed by the requirement that $C = C_0$ at $r = r_0$

$$k_1 = \frac{C_0 \left[1 - \exp - \left(\frac{z \eta}{\phi} \right) \right]}{I_0 \left(\left[\frac{\gamma i_0}{n F \overline{D} C_0} \exp \frac{\alpha z \eta}{\phi} \right]^{\frac{1}{2}} r_0 \right)} \quad (6)$$

$$\text{or} \quad k_1 = \frac{C_0 \left[1 - \exp - \left(\frac{z \eta}{\phi} \right) \right]}{I_0 (\xi)}$$

$$\text{with} \quad \xi = \left[\frac{\gamma i_0}{n F \overline{D} C_0} \exp \frac{\alpha z \eta}{\phi} \right]^{\frac{1}{2}} r_0$$

Thus equation (5) gives the variation of C with the radius of the cylinder (agglomerate) at a given value of x. It is assumed implicitly that the potential E is not a function of r. E (or η) is only a function of x (coordinate in the axis direction) according to Ohm's law:

$$\frac{d\eta}{dx} = -\frac{j(x)}{\pi r_o^2 \overline{\kappa}} \qquad (7)$$

($\overline{\kappa}$ is effective ionic conductivity, j (x) is the current flowing through the electrolyte in the cylinder at the plane (x) and normal to it). At the same time:

$$-\frac{dj(x)}{dx} = 2\pi\gamma \int_o^{r_o} i\, r\, dr \qquad (8)$$

From equations (7) and (8):

$$\frac{d^2\eta}{dx^2} = \frac{2\gamma}{r_o^2 \overline{\kappa}} \int_o^{r_o} i\, r\, dr. \qquad (9)$$

The solution for C (equation (5)) can be used to solve equation (9) for η:
Thus multiplying equation (3) by r d r and integrating gives:

$$\overline{D}\, r_o \left[\frac{\partial C}{\partial r}\right]_{r=r_o} = \frac{\gamma}{nF} \int_o^{r_o} i\, r\, dr \qquad (10)$$

from (9) and (10)

$$\frac{d^2\eta}{dx^2} = \frac{2nF\overline{D}}{\overline{\kappa}\, r_o} \left(\frac{\partial C}{\partial r}\right)_{r=r_o}$$

From solution (5):

$$\left[\frac{\partial C}{\partial r}\right]_{r=r_o} = k_1 \left[\frac{\gamma i_o}{nF\overline{D}C_o}\exp\frac{\alpha z \eta}{\phi}\right]^{\frac{1}{2}} I_o' \left(\left[\frac{\gamma i_o}{nF\overline{D}C_o}\exp\frac{\alpha z \eta}{\phi}\right]^{\frac{1}{2}} r_o\right)$$

$$(11)$$

Also $I_0'(x) = I_1(x)$, where I_1 is the modified Bessel function of order 1. The equation for η is

$$\frac{d^2 \eta}{d x^2} = \frac{2 n F \bar{D} C_0}{r_0^2 \bar{\kappa}} \left[1 - \exp\left(-\frac{z \eta}{\phi}\right) \right] \cdot \frac{\xi I_1(\xi)}{I_0(\xi)} \quad (13)$$

It can be seen that equation (13) expresses η only as a function of x and a series of measurable constants. This equation can be solved with a relatively simple computer program which we have already developed and tested.

With the same computer program the current (j (x)) at different depths of the electrode (including the measurable current at x = o) is found using equation (7), for preset values of the observed external overvoltage.

The local current (i. e. the utilization of the catalyst as function of the coordinates (x, r) of the catalyst particle) can be obtained from equation (1), since we know C (x, r) and η (r) from equations (5) and (13).

In the first computer run for the O_2 reduction on a Pt electrode in 30% KOH at 80°C, assuming agglomerate sizes of 10 μ, we have found currents comparable to those actually measured. A surprising result, however, is that most of the activity was concentrated in the periphery of the agglomerate (with less than 1% penetration).

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